

## MICROSTRUCTURAL AND ANALYTICAL CHARACTERIZATION OF $\text{Al}_2\text{O}_3/\text{Al-Mg}$ COMPOSITE INTERFACES

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**Résumé :** Les propriétés mécaniques d'un matériau composite sont fortement influencées par les réactions se produisant aux interfaces entre les céramiques de renfort et l'alliage de base. Pour un composite  $\text{Al}_2\text{O}_3/\text{Al-Mg}$ , nous nous sommes intéressés à identifier les mécanismes se produisant aux interfaces lors de l'élaboration par squeeze-casting puis après traitements thermiques. Les observations et microanalyses réalisées en MET ont montré que le Mg diffuse vers les interfaces lors de l'élaboration. Des traitements appropriés nous ont permis d'identifier des précipités de  $\text{MgO}$  ou  $\text{MgAl}_2\text{O}_4$  le long de ces interfaces. Enfin, nous avons mis en évidence un durcissement structural de la matrice du composite par précipitation de  $\text{Mg}_2\text{Si}$ .

**Abstract :** Mechanical properties of composite materials are deeply dependent on the chemical and structural reactions taking place at the ceramic-metal interface. This study was devoted to the identification of these mechanisms, in a  $\text{Al}_2\text{O}_3/\text{Al-Mg}$  composite during squeeze-casting and heat treatment. TEM characterization and microanalysis clearly show migration of magnesium to the interface during processing of the composite. Appropriate treatments allowed to identify  $\text{MgO}$  and  $\text{MgAl}_2\text{O}_4$  clusters along the interface. Additionally, mechanical hardening of the matrix by  $\text{Mg}_2\text{Si}$  precipitation was made clear.

### 1 - INTRODUCTION

Aluminium base composites, reinforced by ceramic particles or fibers offer the following improvements :

- an elastic modulus which is significantly higher than that of aluminium (70 GPa).
- a lower coefficient of thermal expansion (c.t.e.) which is closer to that of steel or of cast iron,
- a greater resistance to wear and an improved rupture stress especially at high temperatures.

These are prime requisites for internal combustion engines applications. The interface between the matrix and the reinforcement determines both the as processed composite characteristics and its behavior during its life (thousands of hours). Solidification processing is the preferred manufacturing technique. The proper infiltration of the ceramic network by the liquid, the homogeneity, and the composition of the matrix are governed by the wetting of the reinforcement by the alloy, by the reactions between alloy and ceramic, and by the micro (and macro) segregations that may result of the interphase reactions. The long term behavior and the thermal cycling ( $\text{RT} \leftrightarrow 200^\circ\text{C}$ ) behavior is dictated by the differences in c.t.e. of matrix and ceramic and by the structure of the interface.

Alumina base performs and the squeeze casting process seem to be able to give a satisfactory answer to the requirements of the automotive industry for low production cost, reliability and productivity.

### 2 - MATERIAL

The subject of this study is an aluminium based alloy reinforced with

an alumina fiber perform, made by squeeze casting. An addition of some percent of silica allows to stabilize the crystalline  $\delta$ -structure of the  $\text{Al}_2\text{O}_3$  fibers. Then, the wetting capability of these fibers in the liquid alloy is improved by a colloidal silica coating. The volume reinforcement ratio is 20%. The matrix of the studied composite contains 2% of magnesium.

The interface structure and the precipitation pattern have been studied for different processing steps :

- after squeeze-casting, prior to heat treatment
- after heat treatment (6h-500°C Air quenched),
- after long term heat treatment (100h-500°C) allowing further interface reactions, air quenched.

### 3 - EXPERIMENTAL

Microstructural observations and chemical microanalysis were performed using two complementary techniques :

- TEM/STEM Philips EM 430, equipped with X-ray and EDS spectrometers,
- CAMECA SX 50 microprobe.

Both equipments allowed an accurate identification of the interfacial components, as well as a precise determination of the various segregation products within a few microns from the interface.

TEM thin foils have been ion beam thinned (Ar, 5 Kev) with a low angle of incidence.

### 4 - RESULTS AND DISCUSSION

#### TEM Observations

After the squeeze casting step, microanalysis shows a Mg enrichment at the interfaces, together with  $\text{SiO}_2$ , Si or  $\text{Mg}_2\text{Si}$  inclusions in the same area, identified by EDS, EELS and electron diffraction.

After heat treatment (6h - 500°C),  $\text{Mg}_2\text{Si}$  and Si are still present at the interface, whereas  $\text{SiO}_2$  has been thoroughly reduced. A further Mg segregation is revealed by the concentration linescan in figure 1. Some diffusion of Mg into the fibers will be noticed.

Concurrently, aluminium grains are subject to a mass precipitation identified as  $\text{Mg}_2\text{Si}$ . These precipitates appear like platelets along the  $\langle 100 \rangle$  directions of the matrix (figure 2).

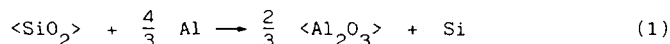
After long term ageing, two more different precipitation forms may be observed along the interface :  $\text{MgO}$  microcrystallites, identified by a ring pattern in electron diffraction, and inclusions (0.1  $\mu\text{m}$  approx.) identified as  $\text{MgAl}_2\text{O}_4$  spinel scattered along the interface. Identification of this spinel was achieved by observing the  $\langle 112 \rangle$  diffraction pattern, where (111) planes permit to distinguish  $\text{MgAl}_2\text{O}_4$  from  $\text{MgO}$  (figure 3) /1, 2, 3/.

Intermetallic compounds of (Al, Fe, Si) ( $\text{FeSiAl}_5$  or  $\text{FeSiAl}_8$ ) about a micron in diameter may be observed as twinned precipitates near the fibers.

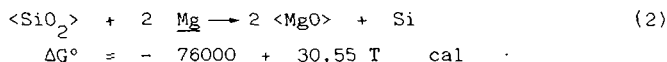
TEM characterization has shown that :

- diffusion of magnesium of the matrix to the interfaces occurs during processing while the aluminium alloy is still in the liquid state, and Mg is trapped near the fibers when the solidification ends. Several chemical reactions may take place at the interface between molten alloy and silica coating of the fibers :

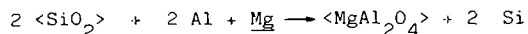
silica reduction by Al and Mg of the alloy :



$$\Delta G^\circ = - 53006 + 11,02 T \quad \text{cal}$$

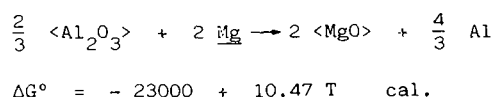


The free enthalpies show that the reduction of  $\text{SiO}_2$  by Mg will prevail, despite its low activity. After a long period of heat treatment, as the activity of soluble Mg will decrease, both reactions will proceed simultaneously, resulting in  $\text{MgAl}_2\text{O}_4$  spinel, according to the following reaction :

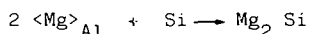


This gives a reasonable explanation for the presence of MgO or  $\text{MgAl}_2\text{O}_4$  at the interfaces.

After complete disappearance of silica, the excess Mg would react on alumina fibers as follows :



- a structural hardening of the matrix after heat treatment. Although such an effect is unexpected in an Al-Mg alloy, the reduction of silica by Al and Mg releases Si which diffuses silicon released at the interfaces from silica reduction by Al and Mg, diffuses through the matrix and precipitates the residual soluble magnesium as  $\text{Mg}_2\text{Si}$  :



So, after liquid reaction with the fibers and silicon segregation, the matrix of the composite is able to precipitation hardened.

#### Microprobe investigations

Aluminium, magnesium, silicon and oxygen concentration linescans have been performed across and between fibres.

Due to experimental limitations the analysed volume is approximately  $2 \mu\text{m}^3$ . This obviously affects quantitative results in the vicinity of matrix-fibers interfaces.

The following assertions may be forwarded :

- the nominal Mg content observed in the matrix of an untreated materials shows a limited segregation during solidification. Additionnally, no diffusion occurs in the fibers.

- the same analysis performed on a treated material shows an important segregation of magnesium at the interface with a concomittent depletion in the matrix (less than 0.3%).

- the silicon content (silica) of the fibers is not affected by the treatment, whereas it significantly increases in the matrix (from 0.2% to 1%). All these results appear on figure 4.

All these results are in good agreement with TEM observations.

#### 5 - CONCLUSION

As a result of the above-mentioned experiments, we may describe the reaction pattern interface as follows :

During processing of the composite, magnesium diffuses towards the interfaces and reacts with the fibers and their silica coating, to form MgO,  $\text{MgAl}_2\text{O}_4$ ,  $\text{Mg}_2\text{Si}$  and Si.

During the heat treatment, magnesium continues to diffuse to the interfaces, and silicon released from those reactions diffuses to the matrix and precipitates Mg to  $\text{Mg}_2 \text{ Si}$  platelets. This process is responsible for the structural hardening of the alloy.

#### ACKNOWLEDGEMENTS

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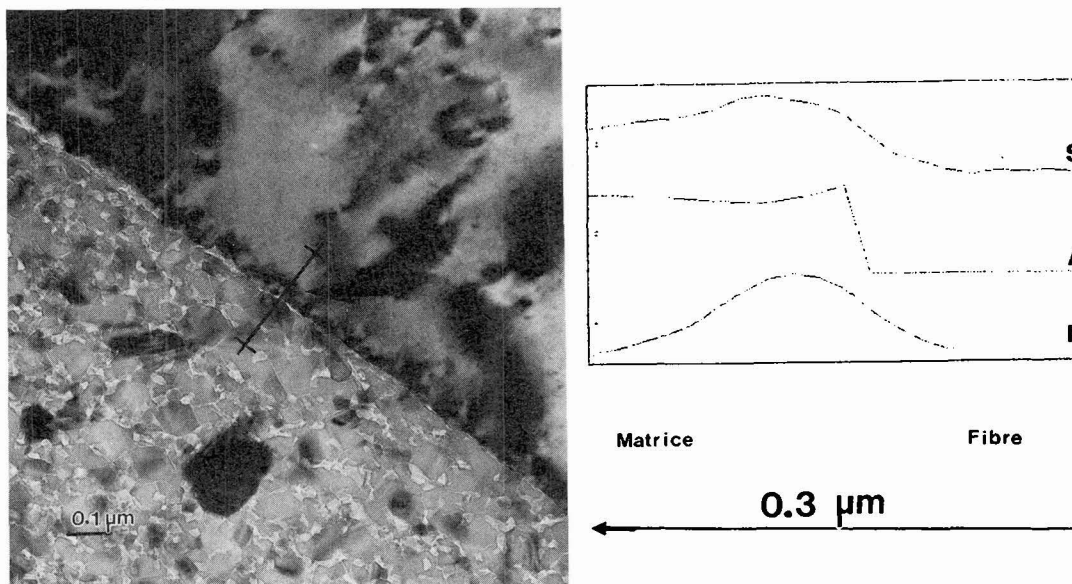


Figure 1 : Concentration linescan through the interface for a treated composite.

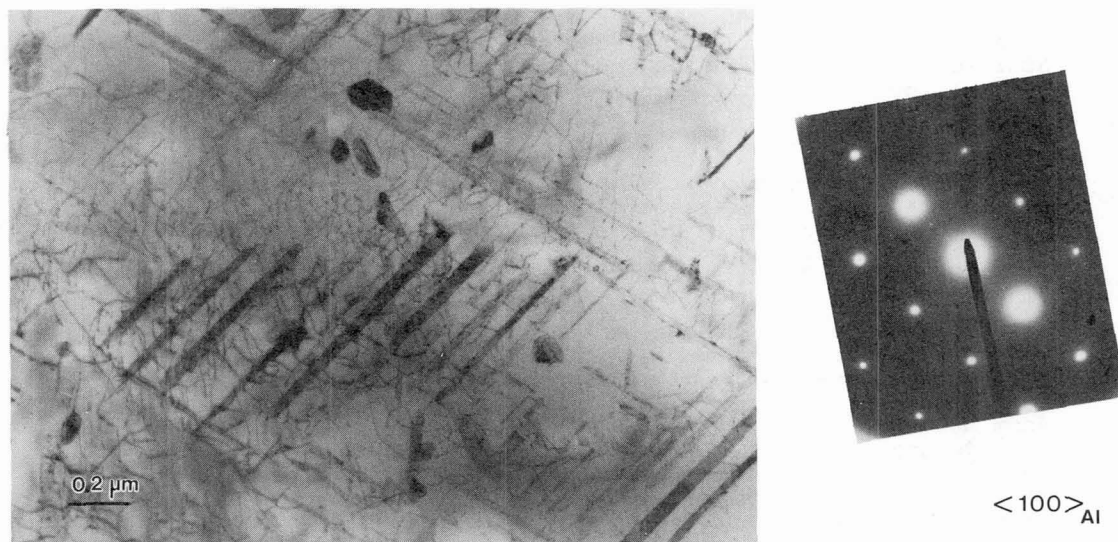


Figure 2 : Matrix precipitation after treatment 6 h - 500°C

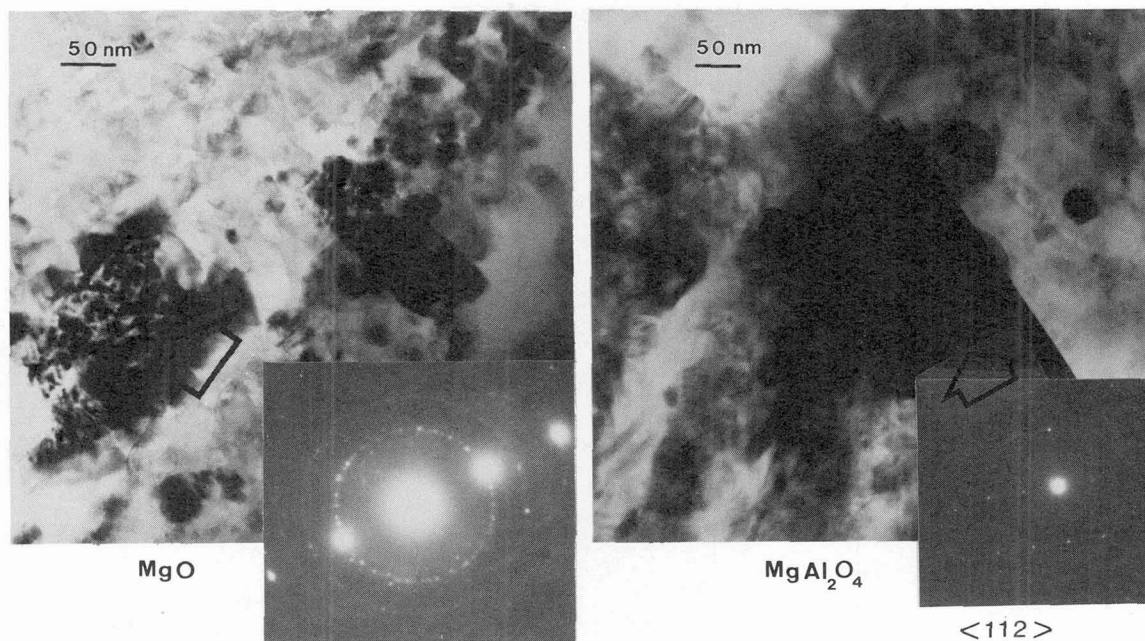


Figure 3 : MgO and MgAl<sub>2</sub>O<sub>4</sub> identification.

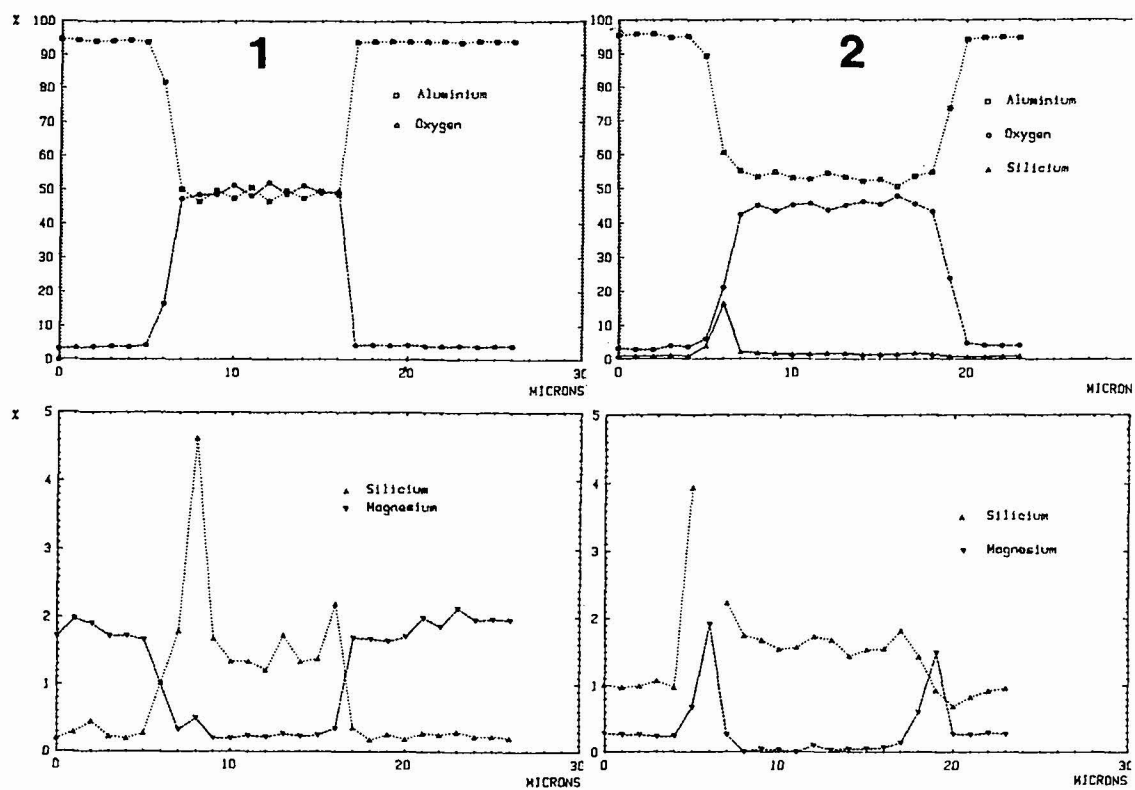


Figure 4 : microprobe linescans. Influence of heat treatment.

- 1) A G 2 not treated
- 2) A G 2 treated